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## Hydrothermal liquefaction of different waste biomass using green solvent 2-methyltetrahydrofuran as extractant and co-solvent<sup>†</sup>

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Hydrothermal processes, such as hydrothermal liquefaction (HTL), are widely used for converting biomass into fuel and chemicals using superheated water as the processing medium. However, conventional organic solvents are often utilized in these processes, raising potential concerns about their environmental impact. For example, dichloromethane (DCM) is commonly used in HTL processes due to its ability to effectively extract organic molecules from the aqueous phase. Alcohols such as ethanol, 1-butanol and non-renewable tetrahydrofuran (THF) have also demonstrated positive effects as a co-solvent with water in biomass conversion. 2-Methyltetrahydrofuran (2-MeTHF) is recognized as a green solvent and is often used as a bio-renewable substitute for DCM and THF in low-temperature transformations. In this comparison study, we explored the potential of 2-MeTHF as a recovery agent and co-solvent in the HTL of several major examples of waste biomass, namely herb residues, paper towel and sawdust. In this investigation, we compare 2-MeTHF with other solvents as extractant and co-solvent in HTL processes. Our research demonstrates that 2-MeTHF is an exceptional option for biocrude extraction, surpassing DCM and consistently producing considerably higher biocrude yields for HTL under several identical conditions (e.g. atmosphere and pH) without lowering the quality of the biocrude products to any significant extent. When utilized as a co-solvent, 2-MeTHF significantly improved biocrude yields, generally outperforming ethanol, 1-butanol and THF while maintaining or enhancing their quality.

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### Sustainability spotlight

This project seeks to enhance the environmental sustainability of hydrothermal liquefaction (HTL), a prevalent method for converting solid waste into renewable fuels and organic chemicals (SDG 7: Affordable and Clean Energy). We specifically explore the use of the bio-renewable solvent, 2-methyltetrahydrofuran, as an extractant or co-solvent in HTL. Our investigation encompasses various biomass types, such as herbal residue, sawdust, and paper waste. While water acts as the primary solvent/reagent in HTL, organic solvents boost product yields or properties. For example, dichloromethane, a common bio-oil extractant, is carcinogenic and ozone-depleting. Our study affirms that 2-methyltetrahydrofuran is a sustainable substitute, enhancing bio-oil yields without compromising product quality. This aligns with UN SDG12 (Responsible Consumption and Production) and SDG13 (Climate Action).

## Introduction

Hydrothermal processing is one of the most important thermochemical methods for converting biomass into fuels and chemicals. In particular, hydrothermal liquefaction (HTL), which involves the conversion of solid biomass into biocrude oil, is adopted by several companies worldwide (e.g., Licella, Genifuel, and Steeper Energy). In a typical HTL process, waste biomass is heated in subcritical water (523–647 K, 4–22 MPa)

with or without catalysts.<sup>1</sup> The main product of HTL is a crude-oil-like liquid organic mixture (biocrude). During HTL, chemical reactions such as hydrolysis, dehydration, reduction, and decarboxylation are catalyzed by ionic species (*i.e.*,  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ ) generated *via* the self-ionization of water. Many of these reactions effectively remove oxygen atoms from the biomolecules, such as carbohydrates and lignin, to form highly deoxygenated organic molecules with elevated energy content. Srokol *et al.* demonstrated that the acid-catalyzed dehydration and base-catalyzed retro-aldol condensation of monosaccharides yielded the major reaction intermediates of carbohydrate HTL (*e.g.*, 5-hydroxymethylfural, furfural, and glycolaldehyde), which further decomposed to generate biocrude.<sup>2</sup> In addition to biocrude, gaseous molecules such as carbon dioxide are also

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produced during HTL. The major advantage of HTL over pyrolysis is that its operating temperature is relatively mild, and it does not require the pre-drying of feedstock. Several studies have investigated the HTL of a vast variety of waste biomass, including wood, food waste and municipal sludge.<sup>3–10</sup>

In addition to water, organic solvents are also commonly employed in HTL. Water-soluble, protic polar organic solvents like ethanol (EtOH)<sup>11–13</sup> and 1-butanol (1-BuOH),<sup>14</sup> glycerol<sup>11,15,16</sup> have been utilized as co-solvents to enhance the biocrude yield during HTL. However, water-insoluble, non-polar solvents like cyclohexane<sup>17</sup> and anisole<sup>18</sup> have been more prevalently employed as co-solvents to improve the separation of biocrude from the aqueous phase. Nonetheless, organic solvents usually serve as extractants for biocrude. Among these, dichloromethane (DCM, Fig. 1) has been extensively used due to its effectiveness in biocrude recovery.<sup>3,19–22</sup> However, DCM is a potential carcinogen and has already been considered an undesirable solvent for pharmaceutical applications.<sup>23</sup> DCM is also unsustainable as it is typically produced from non-renewable sources. Moreover, the increased industrial usage and emission of DCM have been suggested as major contributors to ozone depletion in recent years.<sup>24–26</sup> Therefore, DCM-free HTL processes are preferred to achieve an environmentally friendly process.

Tetrahydrofuran (THF), also depicted in Fig. 1, is a commonly used solvent in industrial and organometallic chemistry. It is predominantly produced *via* the acid-catalyzed dehydration of 1,4-butanediol. THF is a water-miscible liquid and has recently emerged as a promising co-solvent with water for lignocellulosic biomass valorization, as reviewed by Ji *et al.*<sup>27</sup> studies have shown that THF can significantly enhance the yield and selectivity of target products in lignocellulose conversion, such as saccharification and transformation to platform chemicals.<sup>28–30</sup> However, THF is relatively unstable under acidic aqueous conditions.<sup>31</sup> Furthermore, like DCM, this solvent is typically derived from non-renewable sources, highlighting the importance of its recycling for the development of a sustainable biomass valorization process.

2-Methyltetrahydrofuran (2-MeTHF, Fig. 1) is a biomass-derived solvent and fuel that can be produced from two major carbohydrate-based platform chemicals, furfural and levulinic acid, *via* distinct tandem catalytic processes.<sup>31</sup> Its effectiveness as a versatile solvent in low-temperature organic transformations has also been established. Aycock demonstrated 2-MeTHF as an effective, environmentally friendly replacement

for DCM in ambient aqueous/organic biphasic reactions, owing to its low boiling point (80 °C), moderate polarity, and limited water miscibility.<sup>32</sup> 2-MeTHF is also more stable than THF under acidic conditions and more easily recyclable than THF.<sup>31</sup> Biphasic water/2-MeTHF system has been used for the selective fractionation of lignocellulosic biomass and acid-catalyzed hydrolysis of hemicellulose into simple sugars under mild conditions (≤150 °C).<sup>33</sup>

The use of HTL to convert various types of waste biomass has been explored. Some types of biomass, such as Traditional Chinese Medicine (TCM) residue and non-recyclable paper waste, have not received much attention despite their potential due to their large outputs. TCM is a vital component of the well-being of many East Asian regions. In mainland China alone, about 12 million tonnes of TCM herb residues are generated each year.<sup>34</sup> Unfortunately, these residues are usually disposed of in landfills, causing significant environmental damage such as underwater pollution and the release of foul-smelling gas.<sup>35</sup> Furthermore, this practice promotes resource wastage because the herbs could be repurposed. Recently, Guan *et al.* investigated the use of HTL to process TCM herb residues from a pharmaceutical factory using heterogeneous catalysts (*i.e.*, Fe, Ni, and ZSM-5).<sup>36</sup> Overall, TCM residues are well-suited for HTL because of their high moisture content.

The most widely used environmentally friendly methods for treating paper waste are reuse and recycling, such as through hydropulping. However, a significant portion of paper waste cannot be recycled due to contamination, as is often the case with paper used for packaging and sanitary purposes. For instance, in Hong Kong, paper waste accounts for approximately one-quarter of all municipal waste deposited in landfills, second only to food waste.<sup>37</sup> As a result, there is a pressing need for a green technology that can effectively repurpose non-recyclable paper waste.

This study aims to investigate the HTL of three types of waste biomass, specifically paper towel (as a model of non-recyclable paper waste), TCM residue, and pine sawdust, using 2-MeTHF as an auxiliary agent. Initially, the potential of 2-MeTHF as an alternative extractant is explored. This study systematically analyzes and compares the effectiveness of 2-MeTHF as an extractant with that of DCM, which is the most used biocrude recovery agent. Furthermore, this study evaluates the effectiveness of 2-MeTHF as a co-solvent in HTL and compares it with that of THF and other bio-renewable solvents (*i.e.* EtOH and 1-BuOH).

## Results and discussion

### 2-MeTHF as biocrude extractant in HTL processes

**Product yields.** The low process temperature of 270 °C<sup>38</sup> was used in this study due to the relatively low ramp rate of the reactor. The atmosphere has been shown to significantly impact the performance and products of HTL. For example, CO<sub>2</sub> was found to enhance liquid yields and regulate the effect of temperature on biocrude.<sup>39</sup> In this study, the HTL of TCM residue, paper towel, and pine sawdust was conducted in air and CO<sub>2</sub> atmospheres (Table 1). The HTL of pine sawdust was

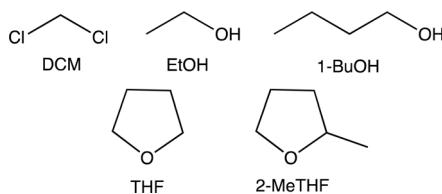


Fig. 1 Solvents of interest: dichloromethane (DCM), ethanol (EtOH), 1-butanol (1-BuOH), tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF).



Table 1 Biocrude yield, mass fractions, atomic ratios and HHVs of bio-oils for HTL with 2-MeTHF or DCM (20 mL  $\times$  3) as the extractant

| Entry           | Substrate    | Extraction solvent | Processing atmosphere | Biocrude (%) | H/C  | N/C  | O/C  | HHV <sup>b</sup> (MJ kg <sup>-1</sup> ) |
|-----------------|--------------|--------------------|-----------------------|--------------|------|------|------|---|
| 1               | TCM residue  | DCM                | Air                   | 10.1         | 0.13 | 0.02 | 0.12 | 39.7                                    |
| 2               | TCM residue  | DCM                | CO <sub>2</sub>       | 10.7         | 0.11 | 0.04 | 0.19 | 34.3                                    |
| 3               | TCM residue  | 2-MeTHF            | Air                   | 11.6         | 0.14 | 0.03 | 0.14 | 38.9                                    |
| 4               | TCM residue  | 2-MeTHF            | CO <sub>2</sub>       | 13.7         | 0.14 | 0.01 | 0.13 | 40.2                                    |
| 5               | Pine sawdust | DCM                | Air                   | 22.8         | 0.09 | 0.0  | 0.37 | 28.1                                    |
| 6               | Pine sawdust | DCM                | CO <sub>2</sub>       | 19.2         | 0.09 | 0.0  | 0.35 | 28.4                                    |
| 7               | Pine sawdust | DCM                | N <sub>2</sub>        | 9.7          | 0.10 | 0.0  | 0.37 | 28.6                                    |
| 8               | Pine sawdust | 2-MeTHF            | Air                   | 28.1         | 0.10 | 0.0  | 0.33 | 29.4                                    |
| 9               | Pine sawdust | 2-MeTHF            | CO <sub>2</sub>       | 30.8         | 0.08 | 0.0  | 0.40 | 26.5                                    |
| 10              | Pine sawdust | 2-MeTHF            | N <sub>2</sub>        | 18.9         | 0.10 | 0.01 | 0.41 | 27.0                                    |
| 11 <sup>a</sup> | Pine sawdust | DCM                | Air                   | 27.9         | 0.10 | 0.0  | 0.35 | 29.3                                    |
| 12 <sup>a</sup> | Pine sawdust | 2-MeTHF            | Air                   | 37.2         | 0.10 | 0.0  | 0.45 | 26.6                                    |
| 13              | Paper towel  | DCM                | Air                   | 16.9         | 0.10 | 0.0  | 0.32 | 30.0                                    |
| 14              | Paper towel  | DCM                | CO <sub>2</sub>       | 24.2         | 0.10 | 0.0  | 0.30 | 30.9                                    |
| 15              | Paper towel  | 2-MeTHF            | Air                   | 23.1         | 0.11 | 0.0  | 0.42 | 27.6                                    |
| 16              | Paper towel  | 2-MeTHF            | CO <sub>2</sub>       | 25.2         | 0.11 | 0.01 | 0.39 | 28.7                                    |

<sup>a</sup> 30 mL of 0.1 M NaOH was used. <sup>b</sup> Higher heating value.

also performed in an N<sub>2</sub> atmosphere, but the biocrude yield was significantly lower than those obtained in air and CO<sub>2</sub> (Table 1). The material recoveries of the HTL of TCM residue, paper towel, and pine sawdust were significantly different. Gasification occurred during the HTL of all of the feedstocks, but most significantly for TCM residue. Gravimetric analysis using a precision balance confirmed that around 70% of products from TCM residue are gaseous ones. CO<sub>2</sub> is established as the main gaseous product in HTL processes.<sup>14</sup> The effects of the extractant on the biocrude, aqueous phase, and insoluble solid residue yields of the HTL of TCM, pine sawdust, and paper are illustrated in Fig. 2. The cumulative yields of these phases are within 8% difference for HTL of repeated runs under identical conditions. For all of the wastes, the HTL process with 2-MeTHF as the extractant resulted in a higher biocrude yield than the

processes with the other extractants, in both CO<sub>2</sub> and N<sub>2</sub> atmospheres. The aqueous phase yields of the HTL of TCM residue, pine sawdust, and paper towel in the presence of 2-MeTHF were either comparable to or lower than those in the presence of DCM; however, the solid residue yields of the HTL of the feedstocks in the presence of 2-MeTHF were significantly lower than those in the presence of DCM. This indicates that 2-MeTHF is more effective than DCM in extracting organic molecules from aqueous and solid phases. This mass balance measurement analysis, coupled with the fact that fewer 2-MeTHF than DCM molecules are present in the same volume of extractant, indicates that 2-MeTHF is more effective than DCM for the dissolution of the depolymerized products of HTL.

To observe the performances of 2-MeTHF and DCM as biocrude extractants for HTL under basic conditions, the HTL of pine sawdust was performed using 0.1 M NaOH solution as the reaction medium (Table 1). Compared with the yields in the presence of water as the solvent, the biocrude and the aqueous phase yields under basic conditions were higher, and the insoluble solid yield was significantly lower, attributable to the reduced repolymerization degree of the depolymerized products in the presence of a base. 2-MeTHF also outperformed DCM to obtain higher biocrude yield under basic HTL conditions.

**Compositions and properties of biocrudes.** The chemical compositions of all the biocrudes obtained *via* extraction with 2-MeTHF and DCM were analyzed. The molecular compositions of the biocrudes obtained were initially analyzed *via* GC-MS (see Tables S1–S3 in ESI†). Owing to the limitations of GC-MS, only the volatile fractions were analyzed. The biocrudes contained various types of compounds, which have been previously reported for other HTL processes.<sup>21</sup> The biocrudes analyzed were found to contain various cycloaliphatic ketones. They are typically formed from the carbohydrate fractions of the waste biomass. Additionally, the biocrudes contained simple lignin-derived phenolics, such as phenol, guaiacol, and syringol. A

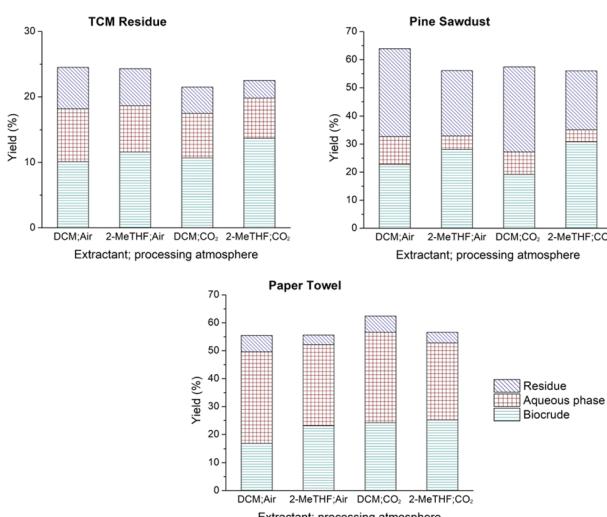


Fig. 2 Product yields of the HTL of TCM residue, pine sawdust, and paper towel with DCM and 2-MeTHF as extractants.



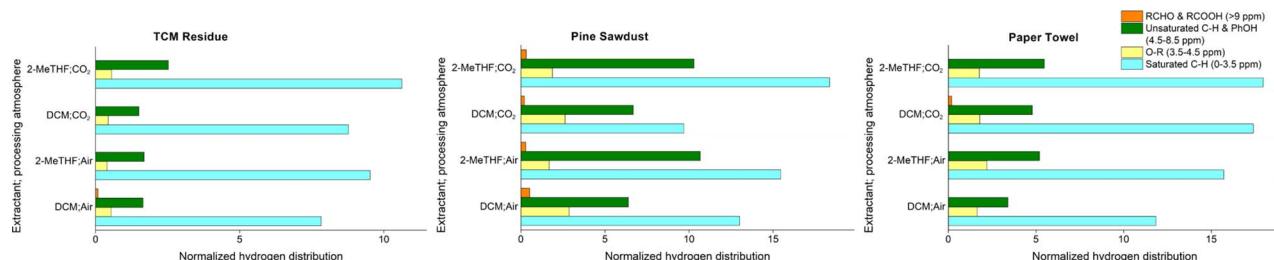


Fig. 3 Normalized hydrogen distributions obtained via semi-quantitative  $^1\text{H}$  NMR analysis of the biocrudes from the HTL of TCM residue, pine sawdust, and paper towel with 2-MeTHF or DCM as the extractant.

wider variety and greater amount of lignin-derived aromatic compounds, such as vanillin, acetovanillone, 4-ethylguaiacol, eugenol, and cresols, were observed in the biocrudes from pine sawdust, likely due to its higher lignin content. The biocrudes from TCM residue contained the widest variety of chemical compounds, including some nitrogen-containing compounds, such as imidazole derivatives, which originated from proteins, and an observable amount of sterol (*e.g.*, cholesterol and stigmasterol) derivatives. Moreover, TCM residue-derived biocrudes also consisted of considerable straight-chain fatty acids. The spectra of chemical compounds in biocrudes derived from DCM and 2-MeTHF are similar, however, GC-MS analysis indicated that 2-MeTHF has the capability to extract more types of aromatic phenolic compounds.

Elemental analysis was conducted to estimate the overall carbon, hydrogen, nitrogen, and oxygen contents of the biocrudes (see Table S4 in ESI $\dagger$ ). Except for the biocrude obtained from TCM residue, the other biocrudes had negligible nitrogen content. The HHVs of the biocrudes were also deduced according to the correlations of eqn (4) reported by Demirbaş.<sup>40</sup> Most of the trials of the HTL of TCM residue with 2-MeTHF as the extractant yielded a higher H/C ratio and lower N/C and O/C ratios than the trials with DCM. Moreover, the HHVs of the TCM residue biocrudes extracted with 2-MeTHF (38.9–40.2 MJ kg $^{-1}$ , Table 1) were slightly higher than those of the DCM-extracted biocrudes (34.3–39.7 MJ kg $^{-1}$ , Table 1). However, the biocrudes of pine sawdust and paper towel waste featured an opposite trend. The HHVs of the sawdust and paper towel biocrudes extracted with 2-MeTHF were 26.5–29.4 MJ kg $^{-1}$  and 27.6–28.7 MJ kg $^{-1}$ , respectively (Table 1), while the HHVs of the DCM-extracted biocrudes were 28.1–29.3 MJ kg $^{-1}$  and 30.0–30.9 MJ kg $^{-1}$ , respectively (Table 1). Overall, the decrease in HHVs was small compared with the enhancement in biocrude yield (see Table S5 in ESI $\dagger$ ).

To investigate the functional group distributions of the biocrudes, a semi-quantitative analysis using  $^1\text{H}$  NMR was performed. A modified version of the chemical shift classifications, originally proposed by He *et al.*,<sup>18</sup> was utilized to estimate these distributions. By integrating peak areas within different regions, the relative abundances of various functional groups in the biocrudes were determined as percentage hydrogen distributions (see Table S6 in ESI $\dagger$ ). The hydrogens were categorized into four classes: saturated C-H (0–3.5 ppm), O-R hydrogens (3.5–4.5 ppm), unsaturated C-H of olefins and aromatics and

phenolic OHs (4.5–8.5 ppm), and aldehyde (RCHO) and carboxylic acid (RCOOH) hydrogens (>9 ppm). Since the depolymerized aromatic products of lignin are mainly phenolic compounds, and that their hydroxyl groups have similar chemical shifts to unsaturated C-Hs, they are put into the same group. The sawdust biocrudes had more unsaturated C-Hs/phenolic OHs than the TCM residue and paper towel biocrudes, attributable to the abundance of lignin in pine wood, which was converted to those phenolic derivatives described earlier. The TCM residue biocrude exhibited the highest proportion of saturated C-Hs (>75%). Saturated aliphatic hydrogens were also the most abundant class of hydrogen atoms in the biocrudes from pine sawdust and paper towel.

Considering both the biocrude yields and percentage distributions of hydrogens derived from semi-quantitative  $^1\text{H}$  NMR data, the normalized hydrogen distributions of the DCM- and 2-MeTHF-extracted biocrudes were evaluated using eqn (5) (Fig. 3). Generally, compared with the DCM-extracted biocrudes, the 2-MeTHF-extracted biocrudes featured higher proportions of saturated and unsaturated C-Hs and phenolic OHs, which were the major types of hydrogens in biocrudes. Recognizable trends were not observed for other classes of hydrogens.

To determine the quantities of various biocrude fractions, the TGA and eqn (6) were used to analyze the normalized boiling point distributions of these fractions (refer to Fig. S1 and S2 in ESI $\dagger$ ). The results showed that the biocrudes extracted using 2-MeTHF contained a larger amount of low-boiling-point fractions, specifically heavy naphtha and kerosene (<271 °C), when compared to those extracted using DCM. Thus, 2-MeTHF displayed good solubility for the small organic molecules derived from biomass depolymerization.

## 2-MeTHF as co-solvent in HTL processes

**Product yields.** 2-MeTHF was employed as the co-solvent (5 or 10 mL) for the HTL of TCM residue, pine sawdust, and paper towel (Table 2). 2-MeTHF was heated with water to test the recovery of this co-solvent under experimental conditions, with or without feedstocks. After extraction with DCM, it was found that near quantitative recovery of co-solvent can be obtained from aqueous phase.

The biocrude yields significantly increased with increasing 2-MeTHF volume from 0 to 10 mL (Fig. 4). The enhancement in the biocrude yields of the HTL of pine sawdust was



**Table 2** Biocrude yield, mass fractions, atomic ratios and HHVs of bio-oils for HTL with 2-MeTHF, THF, 1-BuOH or EtOH as the co-solvent. Processing atmosphere is air. The extraction solvent for the biocrude was DCM (20 mL × 3)

| Entry | Substrate    | Co-solvent (mL) | Biocrude (%) | H/C  | N/C  | O/C  | HHV <sup>a</sup> (MJ kg <sup>-1</sup> ) |
|-------|--------------|-----------------|--------------|------|------|------|---|
| 1     | TCM residue  | —               | 10.1         | 0.13 | 0.02 | 0.12 | 39.7                                    |
| 2     | TCM residue  | 2-MeTHF (5)     | 15.0         | 0.12 | 0.04 | 0.17 | 35.6                                    |
| 3     | TCM residue  | 2-MeTHF (10)    | 18.1         | 0.12 | 0.02 | 0.18 | 36.3                                    |
| 4     | TCM residue  | THF (5)         | 11.8         | 0.13 | 0.04 | 0.19 | 35.9                                    |
| 5     | TCM residue  | 1-BuOH (5)      | 23.4         | 0.11 | 0.06 | 0.21 | 32.6                                    |
| 6     | TCM residue  | EtOH (5)        | 10.8         | 0.12 | 0.04 | 0.18 | 35.4                                    |
| 7     | Pine sawdust | —               | 22.8         | 0.09 | 0.00 | 0.37 | 28.1                                    |
| 8     | Pine sawdust | 2-MeTHF (5)     | 35.4         | 0.11 | 0.00 | 0.28 | 31.9                                    |
| 9     | Pine sawdust | 2-MeTHF (10)    | 50.9         | 0.11 | 0.00 | 0.34 | 29.9                                    |
| 10    | Pine sawdust | THF (5)         | 24.2         | 0.09 | 0.00 | 0.35 | 28.7                                    |
| 11    | Pine sawdust | 1-BuOH (5)      | 30.7         | 0.10 | 0.00 | 0.36 | 28.8                                    |
| 12    | Pine sawdust | EtOH (5)        | 22.1         | 0.08 | 0.00 | 0.35 | 27.8                                    |
| 13    | Paper towel  | —               | 16.9         | 0.10 | 0.00 | 0.32 | 30.0                                    |
| 14    | Paper towel  | 2-MeTHF (5)     | 21.0         | 0.11 | 0.01 | 0.32 | 30.4                                    |
| 15    | Paper towel  | 2-MeTHF (10)    | 29.3         | 0.10 | 0.00 | 0.30 | 30.9                                    |
| 16    | Paper towel  | THF (5)         | 16.9         | 0.10 | 0.00 | 0.30 | 30.3                                    |
| 17    | Paper towel  | 1-BuOH (5)      | 20.4         | 0.10 | 0.00 | 0.37 | 28.5                                    |
| 18    | Paper towel  | EtOH (5)        | 17.0         | 0.10 | 0.00 | 0.36 | 28.8                                    |

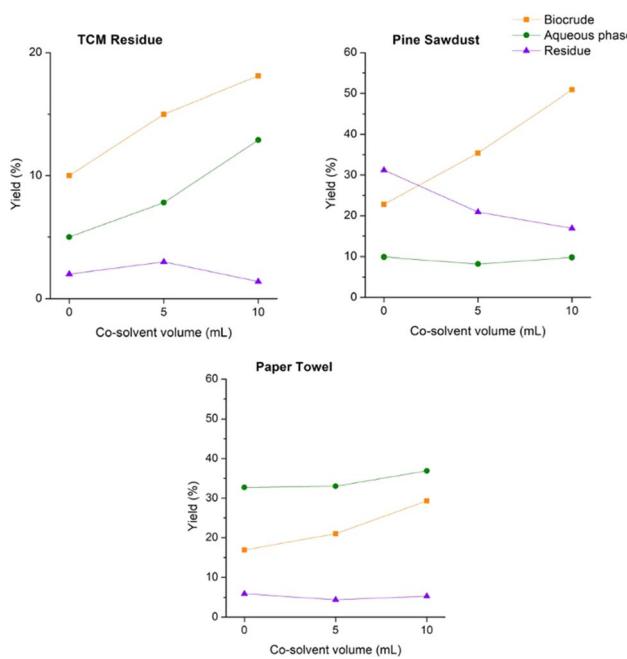
<sup>a</sup> Higher heating value.

accompanied by a significant drop in the amount of solid residue. This was expected, as a previous study reported that in a biphasic 2-MeTHF/H<sub>2</sub>O system, 2-MeTHF could effectively extract lignin and inhibit its repolymerization with other lignin fragments or oligosaccharides, which led to the formation of solid residues.<sup>41</sup>

The HTL of the feedstocks that are less rich in lignin, that is, paper towel and TCM residue, showed essentially no reduction

in the amounts of the aqueous phase and solid residual compounds with the enhancement of the biocrude yield in the presence of 2-MeTHF as a co-solvent. Thus, the biocrude yield enhancement was due to not only effective extraction but also the inhibitory effect of 2-MeTHF on undesirable side reactions (e.g., gasification) in the biphasic reaction system.

The co-solvent performance of 2-MeTHF was also compared with that of THF, 1-BuOH and EtOH (Table 2). Trials with 5 mL of THF, 1-BuOH and EtOH as the co-solvent and TCM residue, sawdust, and paper towel as substrates were conducted. For all of the feedstocks, the trial with 2-MeTHF as the co-solvent resulted in a higher biocrude yield than that with other co-solvents except for the case of using 1-BuOH in TCM residue conversion. This may be due to the incorporation of 1-BuOH with the straight chain fatty acid contents. The results from GC-MS product screening showed that straight chain fatty acids, such as *n*-hexadecanoic acid and oleic acid, were the common products detected from TCM residue HTL. Under high temperature and a proton-rich environment, co-solvent 1-BuOH and carboxylic acids generated during HTL underwent esterification, generating butyl esters. The addition of biocrude weight was caused by an external solvent source. Alternatively, less aqueous phase product and solid residue were recorded for the case of employing 2-MeTHF than using other co-solvents, excluding the case of transforming pine sawdust with 1-BuOH as a co-solvent (Fig. 5). Again, the possibility is that the co-solvent combined with carboxylic acids produced during conversion. Butyl levulinate, which came from the esterification of 1-BuOH and levulinic acid, was identified in GC-MS scanning. With the favor of levulinic acid solubilizing in the aqueous phase, the esterified form was extracted into the organic phase, therefore losing aqueous soluble organics. The use of THF and EtOH as the co-solvent resulted in no significant improvement



**Fig. 4** Product yields from the HTL of TCM residue, pine sawdust, and paper towel with 2-MeTHF as the co-solvent.



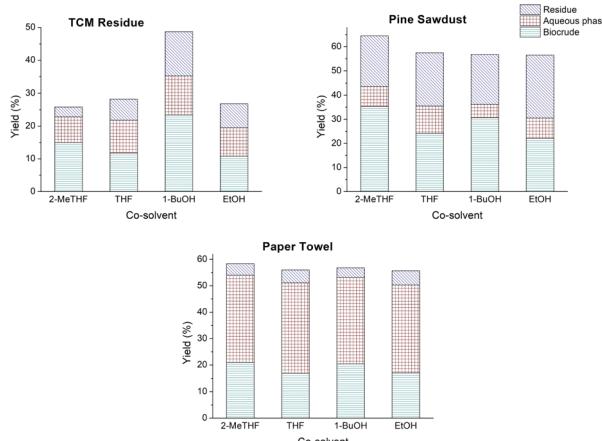


Fig. 5 Comparison of the product yields of the HTL of TCM residue, pine sawdust, and paper towel with 2-MeTHF, THF, 1-BuOH or EtOH as the co-solvents (5 mL).

compared with the cases without a co-solvent (Table 2). However, this was not the case for the use of 1-BuOH. The improved biocrude yields may be an illusion as the co-solvent interacted with carboxylic acids to form esters and the additional butyl chains were included.

It has been reported previously that acid/base-catalyzed reactions occurred during HTL processes, and these could let to both the targeted liquefied and untargeted gaseous and solid residual products. Examples of the side reactions include repolymerization of monomers<sup>42</sup> and retro-aldol condensations<sup>43</sup> to generate gaseous products like formaldehyde, many of which are acid/base-catalyzed. The higher yield in the presence of 2-MeTHF is attributable to the formation of a biphasic system between 2-MeTHF and water at all of the 2-MeTHF/water ratios, which provide space between  $\text{H}_3\text{O}^+/\text{OH}^-$  ions and reaction intermediates.<sup>43</sup> In contrast, THF and water were only immiscible at specific THF/water ratios (*i.e.*, low ratios) and temperature range.<sup>44,45</sup> Thus, other solvents could not shield the intermediates/depolymerized products from side reactions to generate the untargeted products as effectively as 2-MeTHF. As an effective solvent of biocrude, 2-MeTHF could conveniently extract the non-polar products *in situ* during HTL.

**Compositions and properties of biocrudes.** The elemental analysis of biocrudes obtained *via* HTL with co-solvents was conducted. The HHVs of the biocrudes were determined according to the correlations of eqn (4) reported by Demirbaş,<sup>40</sup> as previously described. The HHVs of the biocrudes obtained with 2-MeTHF as the co-solvent (29.9–31.9 MJ kg<sup>-1</sup> for pine sawdust; 30.4–30.9 MJ kg<sup>-1</sup> for paper towel) were higher than those of the biocrudes obtained without a co-solvent (28.1 MJ kg<sup>-1</sup> for pine sawdust; 30.0 MJ kg<sup>-1</sup> for paper towel) (Table 2). However, the trials using TCM waste featured the opposite trend, as the HHV of the biocrude obtained with 2-MeTHF as the co-solvent (35.6 MJ kg<sup>-1</sup>) was lower than that of the biocrude obtained without a co-solvent (39.7 MJ kg<sup>-1</sup>). The HHVs of the biocrudes obtained with 2-MeTHF and THF were roughly similar (35.6 and 35.9 MJ kg<sup>-1</sup>, entries 2 and 4; 31.9 and 28.7 MJ

MJ kg<sup>-1</sup>, entries 8 and 10; 30.4 and 30.3 MJ kg<sup>-1</sup>, entries 14 and 16, Table 2). Moreover, the use of 2-MeTHF made the most energy-rich biocrudes as revealed by comparing the HHVs of using other co-solvents. The biocrude HHVs obtained from 2-MeTHF were overall higher than that of 1-BuOH and EtOH (35.6, 32.6 and 35.4 MJ kg<sup>-1</sup>, entries 2,5,6; 31.9, 28.8 and 27.8 MJ kg<sup>-1</sup>, entries 8,11,12; 30.4, 28.5 and 28.8 MJ kg<sup>-1</sup>, entries 14, 17, 18, Table 2).

Semi-quantitative <sup>1</sup>H NMR was employed to estimate the chemical environments of hydrogen atoms present in biocrudes that were obtained by utilizing 2-MeTHF as a co-solvent. The percentage distribution of hydrogens in the biocrudes (see Table S8 in ESI<sup>†</sup>) was normalized by multiplying with the biocrude yields according to eqn (5) (Fig. 6). For all feedstocks, an increase in the amount of 2-MeTHF co-solvent resulted in consistent increases in the contents of saturated and unsaturated C–H and phenolic OH, whereas no general trends were observed for other types of hydrogens.

The biocrudes from THF, 1-BuOH and EtOH-*co*-solvated HTL were also analyzed *via* semi-quantitative <sup>1</sup>H NMR, and the normalized hydrogen distributions were compared with those of the biocrudes obtained with 2-MeTHF (Fig. S3 in ESI<sup>†</sup>). The biocrudes obtained using 2-MeTHF as the co-solvent contained larger quantities of both unsaturated and saturated compounds than that obtained using THF. The exceptional case was 1-BuOH-*co*-solvated TCM residue HTL. The large increase in saturated C–H corresponded to the butyl chains originating from the co-solvent in ester products.

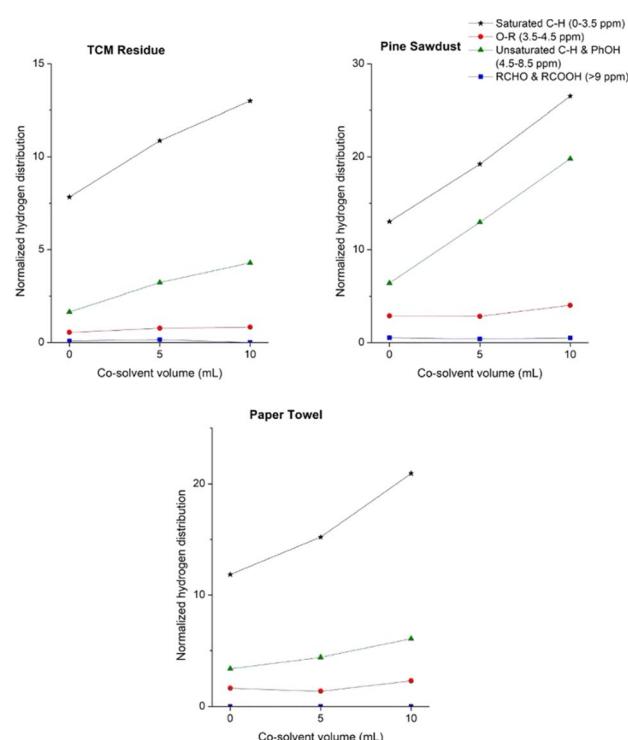


Fig. 6 Results of the semi-quantitative <sup>1</sup>H NMR analysis of the biocrudes obtained from the HTL of TCM residue, pine sawdust, and paper towel with 2-MeTHF as the co-solvent.



The impact of the 2-MeTHF co-solvent on the distribution of biocrude fractions was also investigated (see Fig. S4 in ESI†). When TCM residue was subjected to HTL without a co-solvent, the resulting biocrude was dominated by high-boiling-point fractions, *i.e.*, gas oil and vacuum gas oil (271–538 °C). However, the addition of 5 mL of 2-MeTHF increased the proportion of lighter fractions, *i.e.*, heavy naphtha and kerosene (<271 °C). This enhancement was not sustained with the addition of an additional 5 mL of 2-MeTHF, resulting in a biocrude consisting mainly of heavy fractions. In contrast, biocrudes produced from pine sawdust and paper towels had more significant amounts of lighter oil fractions, regardless of the co-solvent concentration. The biocrudes from pine sawdust and paper towels displayed a higher portion of lighter fractions with increasing co-solvent concentration. Therefore, the incorporation of a specific quantity of 2-MeTHF co-solvent can aid in enhancing both the oil quality and yield.

The distributions of the biocrude fractions obtained with 2-MeTHF, THF, 1-BuOH and EtOH as co-solvents were compared (see Fig. S5 in ESI†). Generally, the biocrudes obtained with 2-MeTHF consisted of a higher proportion of low-boiling-point fractions, that is, heavy naphtha and kerosene (<271 °C). The use of 2-MeTHF as the co-solvent did not significantly enhance the proportion of heavy fractions (*i.e.*, gas oil and vacuum gas oil; 271–538 °C) in the biocrudes, except for the biocrude obtained from pine sawdust. In contrast, the biocrudes from other co-solvated HTL were dominated by heavy fractions. Generally, the use of 2-MeTHF favored the formation of low-boiling-point fractions in the biocrudes, while the use of THF, 1-BuOH and EtOH favored the formation of high-boiling-point fractions, suggesting that biocrudes extracted with 2-MeTHF as the co-solvent possess higher quality.

The chemical composition of biocrudes was also analyzed by GC-MS (see Tables S1–S3 in the ESI†). Using 2-MeTHF as a co-solvent increased the identifiable variety of phenols, with the highest variety observed when 5 mL of 2-MeTHF was added. Phenols and ketones constituted the largest proportion of the product distribution in all the co-solvent experiments. EtOH and 1-BuOH underwent esterification with the carboxylic acid decomposition products of HTL, generating a wide range of new aliphatic products.

## Experimental

### Materials and methods

**Chemical and feedstocks.** DCM and THF were purchased from AQA. THF was distilled to remove inhibitor before use. 2-MeTHF (anhydrous, inhibitor-free) was obtained from Aeros. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was purchased from Dieckmann, and sodium hydroxide was purchased from Sigma-Aldrich.

The TCM residue was obtained from Mr & Mrs Chan Hon Yin Chinese Medicine Specialty Clinic and Good Clinical Practice Centre at Hong Kong Baptist University. This residue was produced *via* typical decoction with water. The composition details of this herb residue (*i.e.*, *Caulis spatholobi* (20 g), *Fructus mori* (15 g), *Radix astragali* (30 g), *Pericarpium citri reticulatae* (9 g), *Fructus jujubae* (15 g), *Semen lablab album* (fried) (20 g),

*Semen raphani* (fried) (15 g), *Radix rehmanniae* (raw) (15 g), *Massa medicata fermentata* (15 g), *Fructus corni* (processed) (15 g), *Poria* (15 g), *Radix pseudostellariae* (20 g), *Fructus hordei germinatus* (15 g), *Semen nelumbinis* (15 g), *Rhizoma atractylodis macrocephalae* (30 g), *Fructus perillae* (15 g), *Endothelium corneum galli gigerii* (15 g)) were provided by the clinic. This herb residue mixture was typical of TCM. A single TCM formula comprises many different plant parts and, occasionally, animal products. The TCM residue consisted of the stems, fruits, roots, rootstalks, fruit peel, seeds, and sprouts of different plants. Some of these components were processed (*i.e.*, fried) before they were mixed with other herbs to prepare the decoction. The TCM residue had a moisture content of 26.6% (determined according to the weight difference between the undried and freeze-dried TCM residue). The residue was blended into powders (2–5 mm) before HTL.

Paper towels were obtained from Sunlight M-Fold Hand Towel. Before HTL, the paper towels were blended into smaller pieces (5–10 mm). Pine sawdust was purchased from Xiao Mao Yang Yang Household and Living Products and converted as received.

**Hydrothermal liquefaction.** HTL experiments were performed in a 0.5 L stainless steel (type 316) stirred batch reactor (Yuhua Instrument & Fan Bo Lun) loaded with 2 g of feedstock and 30 mL of distilled water. Additionally, 5 or 10 mL of co-solvent (2-MeTHF) was added for co-solvent studies. For the experiments in  $\text{N}_2$  or  $\text{CO}_2$ , purging with  $\text{N}_2$  or  $\text{CO}_2$  conducted three times before heating. For experiments performed in air, the initial pressure was 1 atm. For experiments carried out in  $\text{N}_2$  or  $\text{CO}_2$ , the initial pressure was 10 bar. All HTL experiments were conducted at 270 °C, a stirring speed of 600 rpm, and a holding time of 10 min. The terminal reaction pressure ranged from 50 to 80 bar, and about 90 min was required to reach the target temperature.

**Product recovery.** The reactor was cooled immediately after the completion of the reaction in an ice bath. The gas was carefully vented by opening the gas valve and the reactor. All of the materials (solid and liquid) were transferred to a 50 mL centrifuge tube, and the reaction chamber was rinsed with DCM or 2-MeTHF (20 mL). The tube was then filled up to the 50 mL mark with DCM or 2-MeTHF and centrifuged at 4500 rpm for 5 min. The aqueous phase was extracted with DCM/2-MeTHF (2 × 20 mL). For the co-solvent experiments, the extractant was DCM. The combined organic phase and the aqueous phase were separately filtered with two pre-weighed pieces of filter paper. The organic phase was dried with a small amount of  $\text{Na}_2\text{SO}_4$  and then rotary-evaporated at 60 °C. All of the phases were fully oven-dried at 60 °C overnight before yield determination.

**Yield calculations.** The yields of the different phases were determined according to eqn (1)–(3) and expressed in w/w%:

$$\text{Biocrude yield (\%)} = (\text{mass of dried organic phase}) / (\text{initial mass of feedstock}) \times 100\% \quad (1)$$

$$\text{Aqueous dissolved organics yield (\%)} = (\text{mass of dried aqueous phase}) / (\text{initial mass of feedstock}) \times 100\% \quad (2)$$



$$\text{Residue (\%)} = \frac{(\text{mass of dried residue}) / (\text{initial mass of feedstock}) \times 100\%}{(3)}$$

**Higher heating value calculation.** The higher heating values (HHVs) of liquefied products were determined in terms of the carbon, hydrogen, nitrogen, and oxygen (estimated by difference) contents of the bio-oils, according to the correlation reported by Demirbaş:<sup>40</sup>

$$\text{HHV (MJ kg}^{-1}\text{)} = \{33.5[\text{C}] + 142.3[\text{H}] - 15.4[\text{O}] - 14.5[\text{N}]\} \times 10^{-2} \quad (4)$$

**Percentage hydrogen distribution of biocrude.** The percentage hydrogen distributions of biocrudes (in %) were estimated using a modified method of that described by He *et al.*<sup>18</sup> This was performed *via* semi-quantitative <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy. The percentage hydrogen distributions were based on the relative peak areas of different chemical shift regions. The distributions indicated the chemical environments of the hydrogen atoms in the biocrudes.

Biocrude samples (~100 mg) were dissolved in chloroform-d (700 µL), and the samples insoluble in chloroform-d were dissolved in acetone-d<sub>6</sub>. Hydrogen distribution was identified and semi-quantified using a Bruker Ultrashield™ 400 MHz NMR spectrometer. <sup>1</sup>H NMR spectra were acquired under a 30° flip angle, a scan number of 256, and a recycle delay (D1) of 10 s.

**Normalized hydrogen distribution of biocrude.** The normalized hydrogen distributions were calculated as the product of the biocrude yield (eqn (1)) and the percentage hydrogen distribution (see above):

$$\text{Normalized hydrogen distribution} = \text{biocrude yield} \times \text{percentage hydrogen distribution} \quad (5)$$

**Percentage distribution of biocrude fractions.** The normalized distributions of biocrude fractions were calculated as a product of the biocrude yield (eqn (1)) and the distribution of biocrude fractions (see above):

$$\text{Normalized distribution of biocrude fraction} = \text{biocrude yield} \times \text{percentage distribution of biocrude fraction} \quad (6)$$

**Gas chromatography-mass spectrometry (GC-MS).** The chemical compositions of the biocrudes were qualitatively analyzed using an Agilent 6890 N gas chromatograph with 5973 N MSD equipped with a capillary column HP-5MS 30 m × 250 µm × 0.25 µm. Helium was used as the carrier gas. The gas chromatography column temperature was maintained at 50 °C for 5 min and then increased to 300 °C at 5 °C min<sup>-1</sup> and then held for 10 min. The compounds in the biocrudes were compared and identified according to the mass spectral library NIST05.

## Conclusions

We have demonstrated the manifold advantages of utilizing bio-derived 2-MeTHF for thermochemical biomass liquefaction. Our findings reveal that 2-MeTHF, which is a safer alternative to

the potentially carcinogenic and ozone-depleting DCM, is a more potent extractant of biocrude. The yield of biocrude extracted by 2-MeTHF was consistently higher than that of DCM (by 4–95%), even under several identical process conditions and for various feedstocks. This remarkable feat was accomplished with lower concentrations (1 : 1 ratio in volume; 1 : 1.58 in mole) of 2-MeTHF than DCM. The elevated biocrude yield was facilitated by the superior solubility of compounds in 2-MeTHF compared to DCM, where DCM-extracted compounds remained in the aqueous or solid phases. Functional group distribution analysis of the biocrudes revealed enhancements in both saturated and unsaturated organic compounds. TGA results suggest that 2-MeTHF could substantially enhance the extraction of lower-boiling-point fractions. Although the HHVs of 2-MeTHF-extracted biocrudes were generally slightly lower than those of DCM-extracted biocrudes, the benefits of using 2-MeTHF outweigh the slight decrease in HHVs.

Our study also shows that 2-MeTHF holds great potential as a co-solvent for HTL, as it significantly boosts biocrude yields (by 24–123%). This improvement is due to 2-MeTHF's ability to prevent side reactions and extract biocrudes *in situ*. Moreover, when compared to other co-solvents under identical process conditions, 2-MeTHF generally outperforms THF, EtOH, and 1-BuOH—commonly used co-solvents for hydrothermal biomass processing—in enhancing biocrude yields while also enhancing/maintaining HHVs.

## Data availability

The experimental data supporting this research article are included in the ESI.†

## Author contributions

Yuen Wai Lui: investigation, methodology, supervision, validation, visualization, writing – original draft. Sze Ha Tsang: investigation, methodology, validation. Tsz Hin Chan: investigation, methodology, validation. Ka Hei Chan: investigation, validation. Yin Hei Lee: investigation, validation. Hoi Fung Man: investigation, validation. Matthew Y. Lui: conceptualization, funding acquisition, project administration, resources, supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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